

High-Throughput Methane Pyrolysis for Low-Cost, Emissions-Free Hydrogen

Dr. Brad Rupp, PARC Cabot, Modular Chemical, Susteon, Stony Brook University, and Burns Energy Systems

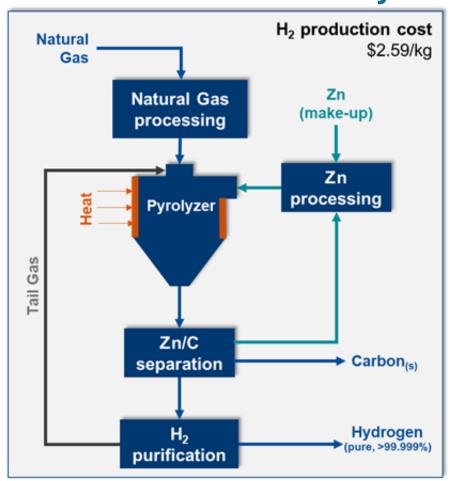
Project Vision

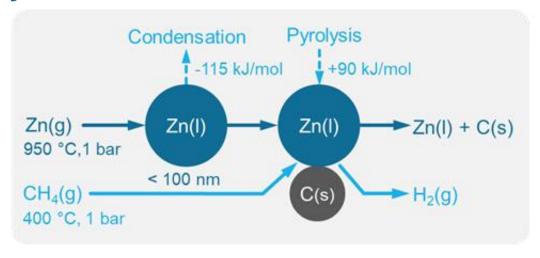
We aim to deliver low cost, emission free hydrogen using a novel condensing liquid metal catalyzed methane pyrolysis reactor that enables modest operating temperatures, high space velocities, and low capital costs

| Total project cost: | \$4.2M |
|---------------------|--------|
| Length | 42 mo. |

The Concept

Zinc condensation catalyzed pyrolysis





Benefits

- High catalytic activity via high surface area
- Integration of vaporization and reaction heats
- Moderate reactor temperatures and pressures
- Simple and effective carbon-metal separation





ARPA-E Methane

Project Objectives

Project Objectives

- Hydrogen productivity
- ► CO₂ emissions
- Carbon market value
- ► Plant (1.5 t/d H₂) economics
- Engineering design for 200 kg/d H₂ pilot plant

Final Project Prototype

- Bench-scale process producing 1 kg/d H₂
- Reactor space velocity > 1,000 h⁻¹
- Single-pass methane conversion > 90%
- Reactor temperature < 1,000 °C</p>
- Carbon separation efficiency > 99 wt% C





 $> 20 \text{ mol/m}^3\text{s}$

< 3.0\$/kg H₂

> 100\$/t

 $< 3 \text{ kg CO}_2/\text{ kg H}_2$

The Team





Brad Rupp Principal Investigator



Mary Louie
Carbon Separation



Jin Ki Hong Process Engineering



Jessy Rivest Project Advisor





Raghubir Gupta
Commercialization
Advisor



Andrew Tong
Bench-Scale Reactor
Development



Vasudev Haribal Process Modeling



Jim Zhou Process Development





The Team





Dane Boysen
Entrepreneur in Residence





Matt Eisaman
Carbon Characterization



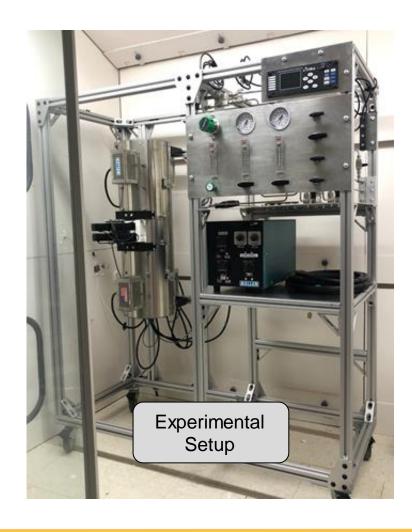


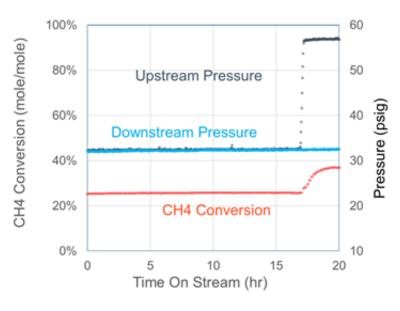
David Matheu
Process Development





Experimental Results







- Understanding zinc condensation behavior
- Have shown long term, steady state operation (20 hrs) at moderate conversion (27%)
- Experiment duration limited by carbon removal
- Reached conversions up to 60% so far

ARPA-E Methane





Carbon Characterization

- No thermodynamic limit on zinc-carbon separability
 - < 5 ppm Zn in carbon powders separated from proxy Zn-C mixtures</p>
- Minimal post-reactor separation expected
 - Current lab process produces carbon product with < 1 wt% Zn without postprocessing
 - ► Other metal impurities at < 100 ppm
- Carbon product has potential to be tailored for useful markets



Pyrolysis Carbon Analysis

| | Concentration (wt%) | | | | | |
|----|---------------------|--|--|--|--|--|
| С | 98.3 | | | | | |
| 0 | 1.24 | | | | | |
| Zn | 0.49 | | | | | |
| Si | 0.006 | | | | | |
| S | 0.003 | | | | | |
| Al | 0.002 | | | | | |
| Fe | 0.002ª | | | | | |
| Cr | 0.0006ª | | | | | |
| Ni | 0.0004ª | | | | | |
| Cu | 0.0002ª | | | | | |

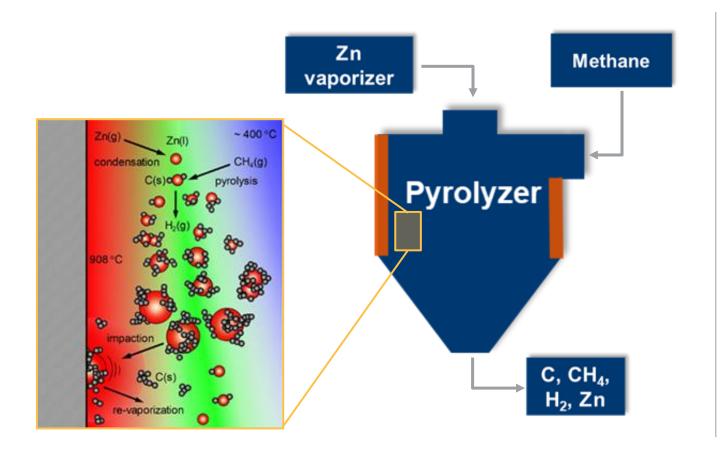
from the XRF

Signal may be largely/solely instrument background





Bench-Scale Unit - 1 kg/day H₂



Designed Operating Conditions

| Temperature, max | °C | 1210 |
|---------------------|--------|------|
| Pressure, max | bar | 9.3 |
| Zinc mass flow, max | kg/day | 4.5 |
| Methane mass flow | kg/day | 4.5 |
| Carbon mass flow | kg/day | 3 |
| Hydrogen mass flow | kg/day | 1 |

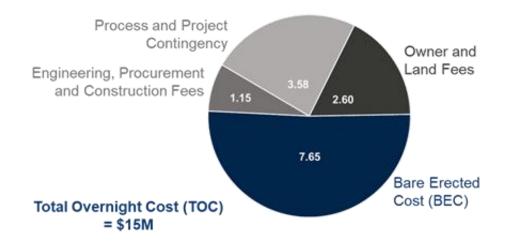
Reactor vessel currently under construction

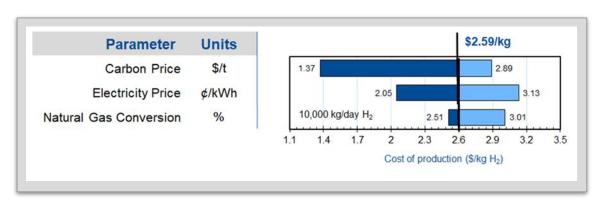




Techno-Economic Analysis

10,000 kg/day H₂ Plant







TEA shows our process can be cost-competitive compared to incumbent technologies





Challenges and Potential Technical Partnerships

Challenges

- COVID-19 has slowed progress
- Commissioning bench-scale reactor slowed due to complexity, finding fabricator, certification process
- Elevated temperature and pressure process requires care and attention for safe operation

Risk Mitigation

External

 Slowed project spending early due to COVID-19 uncertainty

Project

- Continued basic experiments while fabricating reactor
- Carbon analysis to determine value
- Exploring reactor design improvements for improved thermal efficiency and carbon product recovery

Partnerships

- Yes, we're looking for partners!
- Piloting / scale-up
- Carbon utilization

brupp@parc.com dane.boysen@gmail.com

ARPA-E Methane





T2M / Potential Impact

Impact

- Enables low-cost, low-emission hydrogen source
- Feedstock for cleaner carbon end uses

Current Status

- ► TRL 2-3
- Constructing bench-scale prototype
- Evaluating carbon for potential markets

Enabling Success

- Carbon product biggest driver to economic impact
- Understanding market players and needs crucial to scaling
- Engaged with Phillips 66 to potentially utilize carbon product

Industrial **Advisors**











Database - Commercial Methane Pyrolysis Efforts

OBJECTIVE

Keep up to date on the latest developments in methane pyrolysis

- We gather information on all commercial methane pyrolysis efforts
- Currently collect 13 pieces of information (shown at right)
- Database has 22 efforts documented--with more to come
- Plan to update database every quarter

Data Collected

- 1. Start Year
- 2. Company Name
- 3. Location
- 4. Key People
- 5. Funding / Investment
- 6. Technical Approach
- 7. Catalyst / Activator
- 8. Carbon Product
- 9. Process Temp,°C
- 10.Technology Description
- 11.Commercial Status
- 12.TRL
- 13.Website

SAMPLE ENTRIES

| Year Started | Organization Name | Location | Key People | Funding | | Technical Approach | Catalyst or Activator | Carbon Product | Technology Description | Commercial Status | TRL | Website |
|-----------------|-----------------------|-----------------------|--|--|------|-----------------------|--------------------------|------------------------|---|--|-----|--|
| 2010 | Hazer Group | Nedlands (AUS) | Geoff Ward (CEO) Andy Cornejo (CTO, fdr) | \$116,760,000 (mkt cap) Public (ASX:HZR) | 900 | Catalytic | Iron Oxide | Graphite (80- 95%C) | HAZER® Process, iron ore catalyst, produces high purity graphite, fluidized bed reactor, 900 C, | 2019 - Pilot plant 100 kg/d H2 situated in Kwinana, Western Australia | 7 | https://hazergroup.com.au/ |
| 2012 | Monolith Materials | Lincoln NE (USA) | Pete Johnson (fdr), Robert Hanson (CEO, fdr) | \$64,300,000 MHI, Azimuth Capital | 2100 | Plasma | Thermal Plasma | Carbon Black | Thermal plasmas allowing over 5000°C temperatures – licensed technology from Aker Solutions | 2018 - Pilot reactor (2MW) "Seaport" (Redwood City, CA) 2021 - Commercial plant (40 tpd C) "Olive Creek, OC-1" (Hallam, NE) | 10 | https://monolithmaterials.com/ |
| 2012 | BASF | Ludwigshafen (DEU) | Andreas Bode (lead) Dieter Flick | public-private | 1400 | Thermal. | Solid Carbon | Low Grade Carbon | Moving bed of carbon granules with inductive heating | 2014 - Bench scale reactor 2016 - Semi-pilot scale reactor | 5 | https://www.basf.com/global/e n/media/events/2019/basf- research-press; conference.html |



THANK YOU!

Brad Rupp, PhD

brupp@parc.com

Palo Alto Research Center 3333 Coyote Hill Rd Palo Alto, CA 94304



